

PATENT SPECIFICATION

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DRAWINGS ATTACHED

1 210 958

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(54) METHOD AND APPARATUS FOR AUTOMATICALLY CONTROLLING A FUEL CELL

(71) We, ESSO RESEARCH AND ENGINEERING COMPANY, a Corporation duly organised and existing under the laws of the State of Delaware, United States of America, of Elizabeth, New Jersey, United States of America, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention is directed to a method and apparatus for controlling or regulating the concentration of the solute in the solvent of electrolytic solutions. More particularly, the invention is directed to a control apparatus and method for controlling or regulating the amount of an anodically oxidizable organic compound in an electrolytic solution.

Many methods have been suggested heretofore for attempting to monitor the concentration of the solute in a solvent. However, these prior methods are cumbersome and are not sufficiently continuous so as to afford an accurate description of the concentration of the solute in the solvent. In particular, the concentration of the solute is most important in the operation of anodic oxidation processes, such as in the manufacture of chemicals or in the operation of a fuel cell. The concentration in either of such processes, as the anodic oxidation of chemical compounds to produce oxygenated chemical compounds or to produce electricity, is dependent upon the concentration of the compound to be oxidized. It is well-known that in a fuel cell, operating with a liquid electrolyte wherein the fuel is dissolved, that if the concentration becomes quite small, the efficiency of the cell decreases due to the lack of fuel. However, if the concentration is excessive beyond certain limits, then the excess concentration causes a decrease in efficiency due to concentration polarization.

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It has now been found that a relatively simple arrangement may be used to provide highly accurate control of the concentration of the fuel in a fuel cell or the reactants in an anodic oxidation process or to keep a running record of the solute in a solvent which is electrically conductive.

A device for the dual purpose of analyzing and controlling the concentration of fuel in a fuel cell electrolyte is based on the principle that the current carrying capability of a given anode is limited by the concentration of the compound to be oxidized in the electrolyte. All other variables being constant, it is possible to determine the concentration of the compound to be oxidized by simple DC voltage and current measurements. However, electrode condition is a difficult variable to maintain constant. Therefore, steady state measurements that is, measurements which will maintain themselves over long periods of time, do not remain stable particularly with the small electrodes that, of necessity, must be used in an analyzer cell. Stable and reproducible measurements can be obtained under dynamic test conditions by programming the current through a driven cell and measuring the peak current in the system during some portion of a test cycle. The relationship between peak current and concentration of the solute is a constant for each solute. The scanning technique of this invention produces results which are stable to plus or minus 0.5% over a two-hour period. Thus, in accordance with this invention, the operation of a fuel cell consuming a liquid fuel which is miscible with the liquid electrolyte thereof is controlled or regulated by using the current from the fuel cell to produce a linear ramp function current which increases to its maximum value over a selected time interval, whereafter the ramp function current is interrupted for another selected time interval, and the linear ramp

function current is passed through a driven analyzer cell containing the fuel-electrolyte mixture of the fuel cell, fuel being supplied to the fuel cell whenever the voltage drop across the analyzer cell exceeds a predetermined voltage drop.

The scanning technique of this invention using the linear ramp function providing "on" cycle conditions over a period of a number of seconds, and a similar period called the "off" period between each "on" cycle is included in the program of the analyzer. The "off" cycle is an important part of providing analyzer electrode stability. Various time cycles can be used depending upon the characteristics of the particular analyzer system. The preferred "on" and "off" periods are from 35 to 75 seconds, preferably about 50 seconds. Such characteristics would be the current levels, electrode size, concentration range desired or the particular solute being used. In particular, the "off" cycle must be long enough to allow system recovery to conditions which support current during the "on" cycle and are responsive to the solute concentrations in the electrolyte.

Basically, the control system of this invention includes a current scanning cycle which evaluates the performance of the analyzer cell based on reaching a limiting current causing high polarization voltage depending on the solute concentration in the cell. When high polarization occurs, a voltage detector turns on the fuel delivery device for the remainder of the "on" scanning cycle. The level of the current during the "on" scanning cycle is varied by the current demand on the fuel cell. Thus, the fuel concentration level is evaluated based on the current demand on the fuel cell and fuel is added in proportion to the reactant needed.

Referring now to the attached drawings, Figure 1 shows a function of current in relationship to the volume of solute.

Figure 2 is a block diagram of the component parts of the analyzer controller of this invention.

Figure 3 is a circuit diagram of the analyzer controller of this invention.

Referring now to Figure 1, there is shown the relationship between the current and the volume percent of the solute in the electrolyte. The function of current and solute will fall on some line as set forth in the drawing. Peak anodic currents above the line for any given concentration result in severe anode polarization. The triangles mark different values at certain selected percents of solute. This characteristic solute requirement curve to support peak anodic currents can be programmed into the analyzer. When the

current exceeds the value set forth on the line, severe cell polarization occurs and the pump is turned on, fuel is injected and the concentration of the fuel will increase. When the current falls below the line, only normal polarization occurs and the pump will remain off.

Referring now to Figure 2, there is shown a current detector and amplifier 4 which feeds the current from the fuel cell to the current scanning and other electrical components. The scanning generator 5 evaluates the performance of the analyzer cell 1. The cycle generator 8 controls the on-off periods of the cell. Base cycle generator 8 is connected to a DC power source (not shown) through terminals 10 and 11. The DC power may be the fuel cell itself, a battery or other convenient source. The comparator 6 compares the polarization voltage across the analyzer cell 1 with the normal reference level and depending upon whether the cell polarization exceeds or is equal to the normal level actuates or deactivates the pump motor control 7. Pump motor control 7 drives the pump 9. The analyzer cell 1 contains an electrolyte and the solute of the fuel cell. There is shown in Figure 2 the analyzer cell 1 which is a container adapted to retain a liquid and anode 2 and cathode 3 which are both fine platinum wires.

Referring now to Figure 3, there is shown a circuit diagram of the components set forth in the block diagram of Figure 2. Current drain on a DC power source such as a fuel cell is the result of load R_1 and flows through current shunt R_s . The voltage drop across R_s is in the millivolt range and is applied to the emitter-base circuit of transistor Q_1 . This current flow in the emitter-base circuit causes a change in the current flow characteristics of the collector circuit of Q_1 which changes the rate of the charging of ramp capacitor C_1 . This arrangement provides a means for charging capacitor C_1 at a rate proportional to the current through the load R_1 . The base cycle generator set forth in Figure 2 is comprised of components Q_5 , Q_6 and resistors R_8 to R_{15} and capacitors C_2 to C_5 . The base cycle generator of Figure 2, as set forth in the diagram of Figure 3, is a low frequency multivibrator running under repeat cycle conditions of about 30 seconds per half cycle. The multivibrator acts as a control for switching transistor Q_7 . When transistor Q_6 in the multivibrator is nonconducting, there is no voltage drop across the resistor R_9 and thus no current flow through limiting resistor R_{16} and the base-emitter circuit of transistor Q_7 . During the multivibrator half cycle in which Q_6 is conduct-

ing, the voltage drop across resistor R_6 causes current flow through limiting resistor R_{16} and the emitter-base circuit of transistor Q_7 . This causes transistor Q_7 to become very conductive through the emitter-collector circuit and substantially connects "Line A" to the positive side of the DC power line. The positive voltage through Line A provides power for the operation of all functions in the current scanning ramp generator of Figure 2 and voltage comparator and switch of Figure 2. The current scanning ramp generator of Figure 2 comprises the components capacitor C_1 , resistors R_1 and R_2 , transistor Q_8 , resistor R_3 and Zener diode Z_1 . During that portion of the cycle when Line A is connected to the positive side of the power line by the action of Q_7 , the voltage across condenser C_1 is increased at a rate dependent on the collector current of transistor Q_1 . Voltage developed across C_1 causes a current to flow through sampling resistor R_2 and the base-emitter circuit of Q_8 . This current increases the conductive characteristics of the emitter-collector circuit of Q_8 causing current to flow through the analysis cell 1 by a route through R_3 . The cell 1 contains a platinum anode 2 and a platinum cathode 3 along with a sulfuric acid electrolyte and a solute. Electrons flow through the cell 1 by the oxidation of solute at the anode and the liberation of hydrogen at the cathode. The current conduction through the cell has an upper limit which is a function of the solute concentration. When the upper limit of current is exceeded, the voltage drop across the cell increases sharply from the level of about 0.7 to 0.85 volts when the solute is methanol to a voltage of greater than 1.0 volts. The upper limit is established by the minimum conduction voltage of Z_1 minus the drop across Q_8 . The Z_1 minimum conduction voltage may be chosen at some figure such as 2.0 volts and the typical drop across Q_8 is about 0.5 volts which sets the upper limit across the cell 1 at 1.5 volts. The voltage comparator and switch of Figure 2 comprise the components Q_2 , Q_3 , R_{17} , R_3 , R_4 , R_6 , R_7 and D_1 and D_2 . The component parts of the comparator and switch comprise a voltage convertor and switch circuit. D_1 and D_2 are small diodes of preferably germanium so chosen to provide a voltage drop across their series connected terminals of about 0.95 to one volt. The value of limiting resistor R_4 controls the current through diodes D_1 and D_2 and can be used to adjust the desired voltage drop across the two diodes. The voltage level across the two diodes D_1 and D_2 establishes a bias level in the emitter-base circuit of Q_2 such that the transistor Q_2 causes no cur-

rent to flow through resistor R_3 as long as the voltage drop across the cell 1 is less than the bias level. When the voltage drop across the cell exceeds the bias level of Q_2 established by the diodes D_1 and D_2 , current flows through limiting resistor R_{17} and the base-emitter circuit of Q_2 . When the bias level is exceeded, there results a current flow through resistor R_3 and a voltage drop which causes current flow through limiting resistor R_6 and the emitter-base circuit of Q_3 . Current flow then occurs in the emitter-collector circuit of Q_3 through resistor R_7 . The pump motor control and motor of Figure 2 are set forth in the diagram of this Figure by component parts R_{18} , Q_4 and the pump motor. The current flow through R_7 causes a voltage drop which causes current flow through limiting resistor R_{18} and the emitter-base circuit of Q_4 . This results in current flow through the emitter-collector circuit of Q_4 and the DC motor driving the fuel pump. Assuming that the limiting current has occurred and the cell is polarized at some point in the middle of the analysis cycle, the pump will come to the "on" position and continue to deliver fuel to the system until the base cycle generator switches to the "off" part of its cycle. All functions stop due to the lack of conduction of Q_7 and no power being available through Line A during the "off" cycle, the ramp capacitor C_1 discharges to near zero level and the voltage across the cell terminals drops to zero.

Depending upon the rate of fuel injection and the response time of the fuel system on the next analysis cycle, the analyzer cell may either reach limiting current later in the cycle or fail to reach the limiting current. The analysis cycle is when Q_7 is conducting. The later in the cycle limiting current is reached, the less time the pump operates. This operation provides proportional control. Also, if the current demand on the main system increases, the rate of rise of the ramp is increased. This causes the analyzer cell to reach maximum limiting current earlier in the cycle and causes the pump to run longer.

EXAMPLE

The analyzer controller of the instant invention was tested. The control device was assembled in accordance with the diagram set forth in Figure 3. The direct power source was a fuel cell operating with methanol as the fuel. The fuel cell provided the power for the operation of the controller analyzer. Part of the fuel-electrolyte mixture of the fuel cell was fed through and into the analyzer cell 1 of Figure 3. Thirty weight percent sulfuric acid was used as the electrolyte both in

the fuel cell providing the power and in the analyzer cell. The temperature of the operation of both the cell and the analyzer cell was ambient temperature which was about 25°C. The electrodes 1 and 2 of the analyzer cell were platinum black on fine platinum wires. There was about 2 grams of platinum per square foot of electrode surface. The cell was operated and maintained the concentration of the fuel in the fuel cell between the concentration levels of 0.4 to 0.6. The control device of this invention operated efficiently for a prolonged period of time. The scanning cycle used includes on and off periods, each of about 50 seconds duration.

WHAT WE CLAIM IS:—

1. A method of controlling the operation of a fuel cell having a liquid electrolyte and consuming a liquid fuel which is miscible with the electrolyte, in which the current from the fuel cell is used to produce a linear ramp function current which increases to its maximum value over a selected time interval, whereafter the ramp function current is interrupted for another selected time interval, and the linear ramp function current is passed through a driven analyzer cell containing the fuel-electrolyte mixture of the fuel cell, fuel being supplied to the fuel cell whenever the voltage drop across the analyzer cell exceeds a predetermined voltage drop.

2. A method according to Claim 1 in which the two said selected time intervals are each from 35 to 75 seconds.

3. A method according to Claim 1 or Claim 2 in which the two said selected time intervals are substantially equal.

4. A method according to Claim 3 in which the two said time intervals are about 50 seconds.

5. A method according to any preceding claim in which the fuel is methanol and the fuel concentration in the electrolyte is from 0.2 to 0.6 vol.%, the peak current being from 27 to 43 milliamps.

6. A method according to Claim 1 and substantially as hereinbefore described.

7. A method of controlling the operation of a fuel cell substantially as hereinbefore described with reference to the accompanying drawings.

8. Apparatus for controlling the operation of a fuel cell having a liquid electrolyte and which consumes, during operation, a liquid fuel which is miscible with the electrolyte, the apparatus comprising: (a) a current detector and amplifier means connectible through a current shunt to the positive and negative poles of the fuel cell and in series with a current scanning ramp generator means whereby the ramp rate is controlled by the fuel cell current;

(b) a driven analyzer cell containing, during operation, the fuel-electrolyte mixture of the fuel cell and through which current from the ramp generator is passed during operation,

(c) means for comparing the voltage drop across the analyzer cell with a predetermined voltage drop,

(d) a pump means which is actuatable for pumping fuel to the fuel cell in response to a signal from said voltage comparing means indicative of a predetermined degree of polarization of the analyzer cell, and

(e) a base cycle generator means electrically connectible to a source of electrical power which may be the fuel cell, and which at regular intervals activates the current scanning ramp generator means for a selected time.

9. Apparatus for controlling the operation of a fuel cell substantially as described with reference to the accompanying drawings.

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COMPLETE SPECIFICATION

2 SHEETS

*This drawing is a reproduction of
the Original on a reduced scale*

Sheet 1

FIG. 1.

PEAK CURRENT DURING SCANNING CYCLE VS. METHANOL CONCENTRATION

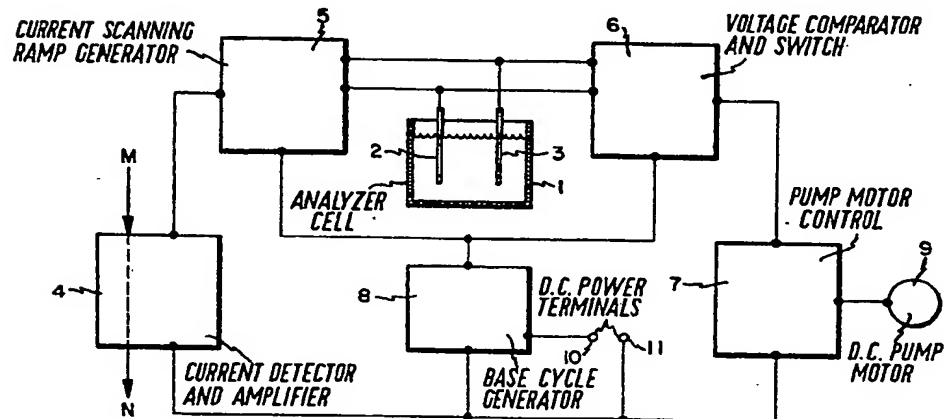
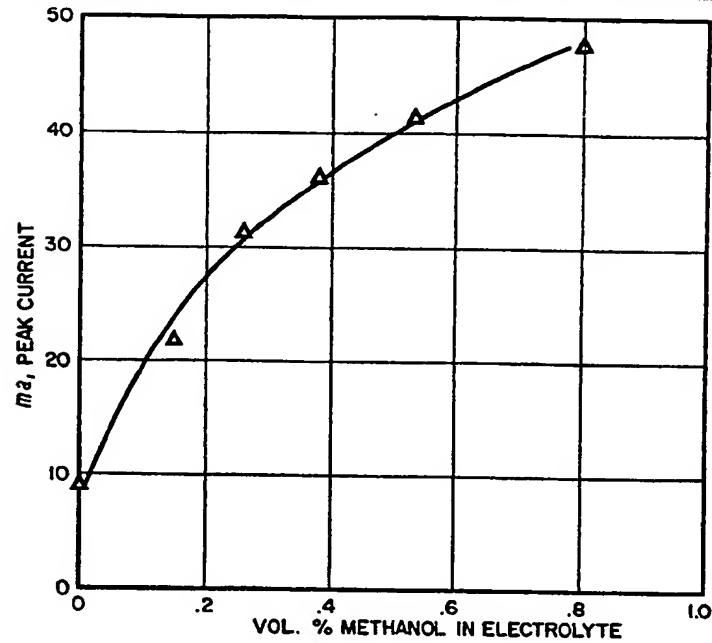


FIG. 2.

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COMPLETE SPECIFICATION

2 SHEETS

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Sheet 2

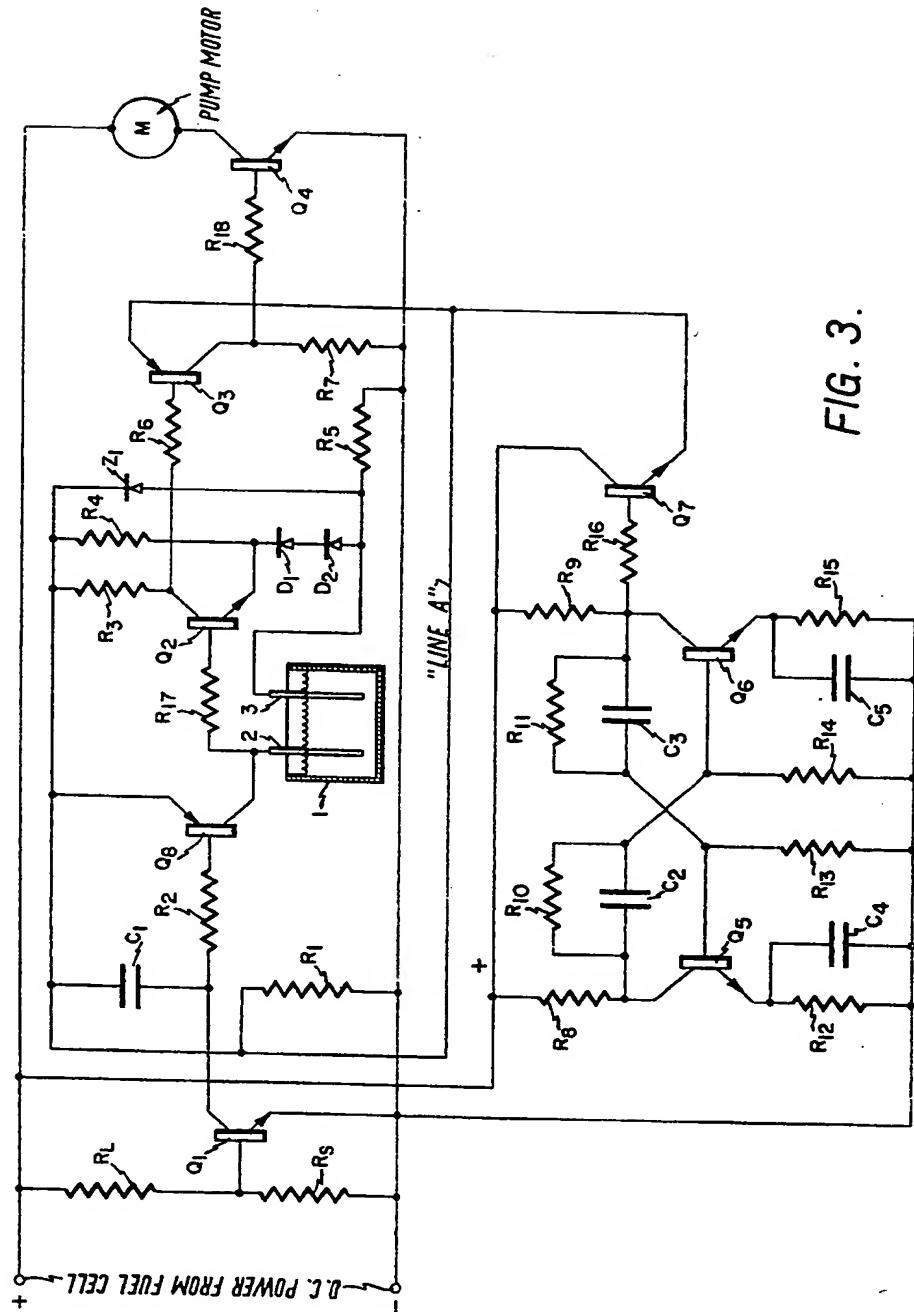


FIG. 3.